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CHEMICAL LASER STUDIES OF CHEMICAL REACTION DYNAMICS. (U)
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FINAL SCIENTIFIC REPORT. 1 Sep 72-31 Jan 76

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Chemical Laser Studies of Chemical Reaction Dynamics

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Abstract

Chemical laser techniques have been used to analyze energy partitioning and chemical reaction dynamics in elementary bimolecular, unimolecular, and photochemical reaction systems. Several new chemical laser systems (e.g., cyanide radical molecular electronic lasers, a hydrogen cyanide polyatomic chemical laser, and a "hot-atom" initiated bimolecular reaction laser) were discovered. A general method for the quantitative determination of product vibrational state distributions was developed and applied to many chemical laser systems. Important rate processes such as specific energy partitioning leading to population inversions plus energy redistribution steps that modify nascent population inversions were determined for operating chemical lasers.

Support experiments in areas of vacuum ultraviolet spectroscopy using a synchrotron radiation source and of tunable intracavity cw dye laser spectroscopy were also carried out.

Certain theoretical approaches toward reaction dynamics were also pursued. A dynamical model for energy partitioning into specific product vibrational states was devised and applied to reaction and relaxation systems. Information theoretic methods were used to analyze patterns of energy partitioning and to predict electronic branching ratios. In addition, ab initio and empirical methods were applied to the computation of potential energy hypersurfaces for chemically reactive systems.

The following report details the above and other accomplishments of our work supported by the Air Force Office of Scientific Research.

I. Project Goals

We analyze published and unpublished work in the context of program goals as summarized from original (first-year) plus renewal proposals:

- 1) extension of chemical laser methodology to the complete determination of product vibronic state distributions
- 2) quantitative determination of product energy content resulting from bimolecular, unimolecular, and photochemical reactions
- 3) vacuum ultraviolet absorption spectroscopy and photochemical reaction product fluorescence measurements
- 4) development of new sub-microsecond flash photolysis equipment
- 5) theoretical approaches toward reaction dynamics
- 6) time-resolved dye laser probing of potential molecular electronic laser systems
- 7) discovery of new chemical laser systems (particularly electronic chemical lasers).

Substantial successes were obtained in meeting and exceeding goals 1 - 3, 5, and 7. Working apparatus was constructed and operated for goals 4 and 6, but detailed experiments were not completed.

II. Summary of Accomplishments

In the following subsections, published papers are referenced according to the numbering sequence used in the Chronological Bibliography contained in Section V at the end of this report.

A) Extension of Chemical Laser Methodology

When the program began, assorted cumbersome and piecemeal techniques (described in Reference 8) were available to extract kinetic information from chemical lasers. We devised a simple grating-tuned cavity technique (described in Reference 1) that permitted the measurement of relative gains of lasing transitions; this information in turn allowed the determination of complete and accurate product vibronic state distributions and of other rate processes such as kinetic isotope effects.

B) Quantitative Determination of Energy Partitioning

Using the grating-tuned cavity technique, we have analyzed numerous chemical laser systems in order to determine features of reaction energy partitioning. Notable accomplishments include: 1) complete analysis of HF and DF product vibronic state distributions generated by the $F + H_2$, D_2 , and HD elementary bimolecular reactions (Reference 1) and 2) complete analysis of HCl photochemical reaction product vibronic state distributions resulting from photolysis of $CH_2 = CHCl$ and other chloroethylenes (Reference 4).

C) Synchrotron Radiation Experiments

We constructed a fully automated absorption and fluorescence spectroscopy apparatus using an intense continuum radiation source (the electron storage ring of the University of Wisconsin Synchrotron Radiation Facility), computer controlled one-meter normal incidence and Seya-Namioka monochromators, photon counting detection, and on-line data acquisition and processing using a PDP-12 computer.

Our apparatus [described in detail in D. E. Klimek, Ph.D. thesis, University of Wisconsin, 1975 (copy sent to AFOSR)], can photoelectrically record VUV (and XUV) spectra of gas phase compounds at $\lambda \geq 200 \text{ \AA}$ with high (digital) accuracy at resolution better than 0.3 \AA , store spectra in digital form, and output hard copies (Calcomp plots). Accurate absorption coefficients can be obtained.

We used the apparatus to measure UV and VUV spectra of interesting photochemical reactants such as chloroethylenes (Reference 4) and cyanides (Reference 5) and to obtain energy partitioning information for the products of photodissociation and predissociation reactions (e.g., electronically excited cyanide radical production, as described in Reference 5). Fluorescence measurements aided in screening potential molecular electronic chemical laser systems.

D) Development of Sub-Microsecond Flash Photolysis Equipment

We have constructed a linear array of flashlamps that produces a fast (100 - 200 nanosecond risetime, depending on lamp construction), broadband ($\lambda \geq 1500 \text{ \AA}$), high-intensity (500 - 600 J stored electrical energy is discharged through the array) photolysis source in a configuration suitable for chemical laser generation. Many known chemical laser systems (I^* , CN^* , HF , etc.) have been operated readily in this device; several candidate electronic lasers have thusfar failed to produce real lasers with this equipment.

E) Theoretical Approaches Toward Reaction Dynamics

We have registered a number of accomplishments: 1) invention of an intuitively satisfying dynamical model that predicts product vibronic state distributions in many reaction and relaxation rate processes such as bimolecular reactions (Reference 3) and photochemical reactions (References 4 - 5), 2) application of information theoretic methods to the analysis of reaction energy partitioning (References 1 and 4) and to the prediction of electronic branching ratios (Reference 6), 3) computation

of ab initio potential energy hypersurfaces for HFCO [described in D. E. Klimek, Ph.D. thesis, University of Wisconsin, 1975 (copy sent to AFOSR)] and for the CN + H₂ bimolecular reaction system [described in G. A. West, Ph.D. thesis, University of Wisconsin, 1975 (copy sent to AFOSR)], and 4) invention of an empirical potential energy hypersurface for bimolecular reaction systems (Reference 10).

F) Dye Laser Spectroscopy

We have had considerable success in obtaining spectra of highly-forbidden optical transitions by dye laser quenching (Reference 12) and by photoacoustic detection (K. V. Reddy, Ph.D. thesis, in preparation) techniques. Dye laser methodology has been extended to transient measurements (Reference 11), culminating in the first observation of the cyanide radical $B^2\Sigma \leftrightarrow A^2\Pi$ system in absorption (K. V. Reddy, ibid.). Applications to identification of optical gain in potential electronic chemical laser systems have been made, but candidates scrutinized [O*(¹S), SnO*] have not exhibited gain (K. V. Reddy, ibid.).

G) Discovery of New Chemical Laser Systems

We have discovered over forty new chemical lasers based upon bimolecular, unimolecular, and photochemical reactions. The most notable systems are: 1) a "hot-atom" chemical laser (Reference 2), 2) cyanide radical molecular electronic chemical lasers (Reference 5), and 3) the HCN polyatomic chemical laser (Reference 9).

H) Other Accomplishments

Certain work related to the primary project goals was completed under AFOSR support: 1) a kinetic spectroscopy and pulse radiolysis study of the reaction rates of vibrationally excited cyanide radicals with molecular hydrogen [G. A. West, Ph.D. thesis, University of Wisconsin, 1975 (copy sent to AFOSR)], 2) reviews on

dynamical studies employing chemical lasers (Reference 8) and lasers in general (Reference 7), and 3) measurements of photochemical and bimolecular reaction branching ratios (References 1 and 4) and of collisional energy redistribution processes such as electronic-to-vibrational energy transfer (Reference 1) and internal conversion in cyanide radical (Reference 5).

III. Personnel Supported and Degrees Completed

Eleven graduate students and three postdoctoral associates have benefitted from AFOSR research support:

A) Postdoctoral Associates

Dr. Robert G. Bray

Dr. Oded Kafri

Professor J. Thomas Knudtson

B) Doctoral Degree Recipients

Dr. Daniel E. Klimek

Dr. Gary A. West

C) Doctoral Candidates

Mr. Sherwin T. Amimoto

Mr. Steven N. Bittenson

Mr. Bret D. Cannon

Ms. Julianne C. Elward

Mr. Robert J. Gill

Mr. Kammalathinna V. Reddy

D) Master's Degree Recipients

Mr. Wolfgang Henke

Mr. Stephen K. Liu

Mr. William A. Tricomi, Jr.

IV. Presentations on AFOSR-Related Projects

A) Grant Period (9/1/72 - 8/31/76)

- 1) Eighth Middle Atlantic Regional Meeting, American Chemical Society, Washington, D.C., January 17, 1973 - "The Haloethane Photochemical Lasers: Vibrational Energy Content of the Hydrogen Halide Photolysis Products."
- 2) Solid State Physics Seminar, Department of Physics, University of Wisconsin, Madison, Wisconsin, March 14, 1973 - "Photochemical Lasers."
- 3) Departmental Colloquium, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, March 21, 1973 - "Chemical Laser Studies of Chemical Reaction Dynamics."
- 4) Chemistry Seminar, Argonne National Laboratory, Argonne, Illinois, April 23, 1973 - "Intimate Details of Photochemical Reactions Revealed by Chemical Lasers."
- 5) James Franck Institute Colloquium, University of Chicago, Chicago, Illinois, April 24, 1973 - "Intimate Details of Bimolecular Reactions Revealed by Chemical Lasers."
- 6) Gordon Research Conference on Molecular Electronic Spectroscopy, Proctor Academy, Andover, New Hampshire, August 2, 1973 - "Spectroscopy and the Dynamics of Photochemical Reactions."
- 7) NATO Advanced Study Institute on Vacuum Ultraviolet Spectroscopy and Photochemistry, Far Hills Inn, Val Morin, Quebec, Canada, August 14, 1973 - "Are Spectroscopy and Photochemistry Intimately Inter-related?"

- 8) American Chemical Society 166th National Meeting, Chicago, Illinois, August 30, 1973, three papers in the Division of Physical Chemistry sessions:
 - a) Paper 98 - (Physical Chemistry) "Complete HF Vibrational State Populations Produced by the $F + H_2$ Reaction."
 - b) [Co-authored with G. A. West] Paper 100 (Physical Chemistry) - "Cyanide Radical Electronic and Vibrational Photodissociation Lasers."
 - c) [Co-authored with G. A. West] Paper 101 (Physical Chemistry) - "A Polyatomic Chemical Laser: Vibrationally Excited Hydrogen Cyanide from the $CN + H_2$ Bimolecular Reaction."
- 9) Departmental Colloquium, Department of Chemistry, Columbia University, New York, October 4, 1973 - "Chemical Laser Studies of Chemical Reaction Dynamics."
- 10) Air Force Office of Scientific Research Conference on Molecular Electronic Chemical Lasers, Kirtland AFB, October 12, 1973 - " $CN^*(A^2\Pi)$ Molecular Electronic Photodissociation Lasers."
- 11) Sixth Annual Synchrotron Radiation User's Group Meeting, Physical Science Laboratory, University of Wisconsin, Stoughton, Wisconsin, October 22, 1973 - "Photochemistry and Spectroscopy of Formyl Fluoride." (with D. E. Klimek)
- 12) Israel Scientific Research Conference on Molecular Energy Transfer, Ein Bokek, Israel, December 18, 1973 - "Chemical Laser Studies of Energy Partitioning into Chemical Reaction Products."
- 13) Departmental Colloquium, Department of Chemistry, Tel-Aviv University, Tel-Aviv, Israel, December 26, 1973 - "Chemical Laser Studies of the Dynamics of Photochemical and Unimolecular Reactions."

- 14) American Chemical Society 167th National Meeting, Los Angeles, California, April 3, 1974 - "The Chloroethylene Photochemical Lasers: Vibrational Energy Content of the HCl Molecular Elimination Products."
- 15) VIIIth International Quantum Electronics Conference, San Francisco, California, June 11, 1974 - "Chemical Laser Studies of Unimolecular Reaction Dynamics" (with Eric Sirkin).
- 16) 29th Annual Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 11, 1973 - "Vacuum Ultraviolet Absorption Spectrum of HFCO" (with D. E. Klimek).
- 17) 11th Informal Conference on Photochemistry, Nashville, Tennessee, June 18, 1974 (2 papers):
 - a) "Fluoroethylene Photoelimination Chemical Lasers: Observed HF Vibrational Transitions and Measured HF Vibrational State Populations" (with W. A. Tricomi, Jr.).
 - b) "Electronic and Vibrational Lasers from the Photodissociation of Parent Cyanides and an HCN Polyatomic Laser from the Reaction: $\text{CN} + \text{H}_2$ " (with G. A. West).
- 18) 1st Summer Colloquium on Electronic Transition Lasers, Santa Barbara, California, June 18, 1974 - "Golden Rule Calculation of Reaction Product Vibronic State Distributions."
- 19) Dynamics of Molecular Collisions Conference, Santa Cruz, California, July 29 - August 1, 1974 (2 presentations):
 - a) "Energy Disposal and Energy Requirements in Polyatomic Bimolecular Reaction Systems."
 - b) "Ramifications of Vibronic Reaction Surprisals."

- 20) Departmental Seminar, Department of Chemistry, University of Texas, Austin, Texas, August 9, 1974 - "Chemical Laser Studies of Photochemistry."
- 21) Gordon Research Conference on Atomic and Molecular Interactions, Wolfeboro, New Hampshire, August 16, 1974 - "Decays of Resonances."
- 22) Conference on Radiationless Processes, Schliersee, West Germany, September 12, 1974 - "Photodissociative and Predissociative Excitation of the Cyanide Radical."
- 23) Physical Chemistry Seminar, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota, September 30, 1974 - "Chemical Laser Studies of Photochemical Reaction Dynamics."
- 24) 4th Conference on Chemical and Molecular Lasers, St. Louis, Missouri, October 21, 1974 - (2 papers):
 - a) "Cyanide Radical Photodissociation and Predissociation Chemical Lasers: Molecular Electronic and Vibrational Laser Emissions" (with G. A. West).
 - b) "Chloroethylene Photochemical Lasers: Vibrational Energy Content of the HCl Molecular Elimination Products."
- 25) Franck Colloquium, James Franck Institute, University of Chicago, Chicago, Illinois, November 19, 1974 - "Non-Statistical (i.e., Dynamical) Effects in Unimolecular and Photochemical Reactions."
- 26) Chemistry Seminar, Department of Chemistry, University of Illinois, Chicago, Illinois, November 26, 1974 - "Chemical Laser Studies of Photochemistry."
- 27) American Physical Society Division of Electron and Atomic Physics, Chicago, Illinois, December 4, 1974 - "Time- and Wavelength-Resolved Spectra of Pulsed Chemical Lasers."

- 28) Workshop on Computation in Chemistry, Argonne National Laboratory, Argonne, Illinois, January 24, 1975 - "Chemical Reaction Dynamics."
- 29) 5th Winter Colloquium on Quantum Electronics, Snowmass, Colorado, February 4, 1975 - "CN Molecular Electronic Chemical Lasers."
- 30) AFOSR Contractor's Meeting, Kirtland AFB, New Mexico, June 3, 1975 - "Cyanide and Other (Potential) Molecular Electronic Chemical Lasers."
- 31) Seminar on Collisions Involving Excited Potential Hypersurfaces, Orsay, France, August 5, 1975 - "Analysis of Electronically Non-adiabatic Chemical Reactions: An Information Theoretic Approach" (with U. Dinur, R. Kosloff, and R. D. Levine).
- 32) American Chemical Society National Meeting, Chicago, Illinois, August 28, 1975 - "Reaction Rates of Vibrationally Excited Cyanide Radicals with Molecular Hydrogen" (with G. A. West, S. Gordon, and W. Mulac).
- 33) Department of Chemistry Colloquium, Case Western Reserve University, Cleveland, Ohio, September 11, 1975 - "HCN Polyatomic Chemical Laser."
- 34) Department of Chemistry, Brown University, Providence, Rhode Island, September 19, 1975 - "HCN Polyatomic Chemical Laser."
- 35) Eighth Annual Synchrotron Radiation User's Group Meeting, Stoughton, Wisconsin, October 21, 1975 - "Absorption and Fluorescence Spectra of Formyl Fluoride" (with S. Amimoto and D. E. Klimek).
- 36) Joint Chemistry Colloquium, Departments of Chemistry, Harvard University and MIT, Cambridge, Massachusetts, October 23, 1975 - "Dynamics of the $CN + H_2$ Reaction."
- 37) First Chemical Congress of the North American Continent, Mexico City, Mexico, December 2, 1975 - "The Electronic Structure of Formyl Fluoride" (with D. E. Klimek, G. Das, and A. C. Wahl).

- 38) American Physical Society Meeting, New York City, February 2, 1976 -
"The New Alchemy: Laser Selective Excitation of Bimolecular Reactants."
- 39) Physical Chemistry Seminar, Wayne State University, Detroit, Michigan,
February 5, 1976 - "Dynamics of the $\text{CN} + \text{H}_2$ Reaction."
- 40) Conference on Gas Kinetics, University of Texas, Austin, TX, March 17,
1976 - "The New Alchemy: Laser-Induced Chemistry."
- 41) Corporate Research Center, Exxon Corporation, Linden, New Jersey,
March 24, 1976 - "Laser Chemistry."
- 42) Physical Chemistry Seminar, Department of Chemistry, University of
Illinois, Urbana, Illinois, April 14, 1976 - "Chemical Laser and
Other Studies of $\text{CN} + \text{H}_2$ Reaction Dynamics."
- 43) Physical Chemistry Seminar, Department of Chemistry, Ohio State
University, Columbus, Ohio, April 26, 1976 - "Chemical Laser and
Other Studies of $\text{CN} + \text{H}_2$ Reaction Dynamics."
- 44) 31st Symposium on Molecular Spectroscopy, Ohio State University,
Columbus, Ohio, June 14, 1976 - "Measurements of Highly-Forbidden
Optical Transitions by cw Dye Laser Spectroscopy" (with R. G. Bray,
W. Henke, S. K. Liu, and K. V. Reddy).
- 45) IX International Quantum Electronics Conference, Amsterdam, The
Netherlands, June 16, 1976 - "A Polyatomic Chemical Laser:
Vibrationally Excited Hydrogen Cyanide Produced by the $\text{CN} + \text{H}_2$
Bimolecular Reaction" (with G. A. West).
- 46) 31st Symposium on Molecular Spectroscopy, Ohio State University,
Columbus, Ohio, June 18, 1976 - 2 papers:
 - a) "Fluorescence Quantum Yields of Single Vibronic Levels of
Formyl Fluoride and Vibronic State Distributions of Photo-
eliminated Hydrogen Fluoride" (with S. Amimoto).

- b) "Polyatomic Overtone and Combination Band Spectroscopy by Intracavity Dye Laser Quenching". (with S. K. Liu and K. V. Reddy).

- 47) Gordon Research Conference on Dynamics of Molecular Collisions, Holderness School, Plymouth, New Hampshire, July 27, 1976 - "Laser Studies of Reaction Dynamics."

B) Post Grant Period (after 9/1/76)

- 48) Third Summer Colloquium on Electronic Transition Lasers, Snowmass, Colorado, September 9, 1976 - "An Intracavity Dye Laser Technique for Spectroscopic and Kinetic Measurements of Transients" (with R. G. Bray, W. Henke, S. K. Liu, and K. V. Reddy).
- 49) Bell Telephone Laboratory, Murray Hill, New Jersey, September 22, 1976 - "Dynamics of the $CN + H_2$ Reaction".
- 50) Departmental Colloquium, Department of Chemistry, Columbia University, New York, New York, December 2, 1976 - "Dynamics of the $CN + H_2$ Reaction".
-
- 51) Second Winter Colloquium on Laser Induced Chemistry, Park City, Utah, February 15, 1977 - "Intracavity Laser Photoactivation."
- 52) American Chemical Society 173rd National Meeting, New Orleans, Louisiana, March 23, 1977 - "Intracavity Dye Laser Photoactivation."
- 53) American Chemical Society North Jersey Section Meeting, Seton Hall University, South Orange, New Jersey, March 28, 1977 - "Laser Alchemy."
- 54) 5th Conference on Chemical and Molecular Lasers, St. Louis, Missouri, April 18, 1977 - (4 papers):
- a) "Investigation of Visible Electronic Chemical Lasers and Transients by Intracavity Dye Laser Techniques" (with K. Reddy).
- b) "The Formyl Fluoride Photochemical Laser: Chemical Laser Determination of the HF Vibrational State Distributions" (with S. Amimoto).

- c) "Chemical Laser Determination of Product Vibrational State Populations for the Halogen Atom + Hydrogen (Deuterium) Halide Reactions" (with S. Bittenson).
- d) "A Hydrogen Cyanide Chemical Laser" (with G. A. West).

V. Chronological Bibliography and Abstracts of PublicationsA) Bibliography

- 1) M. J. Berry, "The $F + H_2$, D_2 , HD Reactions: Chemical Laser Determination of the Product Vibrational State Populations and the $F + HD$ Intramolecular Kinetic Isotope Effect," J. Chem. Phys., 59, 6229 (1973).
- 2) M. J. Berry, "Hot-atom Initiated Chemical Laser Study of the $H^* + SF_6$ Reaction," Chem. Phys. Letters, 22, 507 (1973).
- 3) M. J. Berry, "Golden Rule Calculation of Reaction Product Vibronic State Distributions," Chem. Phys. Letters, 27, 73 (1974).
- 4) M. J. Berry, "The Chloroethylene Photochemical Lasers: Vibrational Energy Content of the HCl Molecular Elimination Products," J. Chem. Phys., 61, 3114 (1974).
- 5) G. A. West and M. J. Berry, "CN Photodissociation and Predissociation Chemical Lasers: Molecular Electronic and Vibrational Laser Emissions," J. Chem. Phys., 61, 4700 (1974).
- 6) U. Dinur, R. Kosloff, R. D. Levine, and M. J. Berry, "Analysis of Electronically Nonadiabatic Chemical Reactions: An Information Theoretic Approach," Chem. Phys. Letters, 34, 199 (1975).
- 7) M. J. Berry, "Laser Studies of Gas-Phase Chemical Reaction Dynamics," Ann. Rev. Phys. Chem., 26, 259 (1975).
- 8) M. J. Berry, "Chemical Laser Studies of Energy Partitioning into Chemical Reaction Products," in R. D. Levine and J. Jortner (editors), Molecular Energy Transfer (Wiley, New York, 1976).
- 9) G. A. West and M. J. Berry, "A Polyatomic Chemical Laser: Vibrationally Excited Hydrogen Cyanide Produced by the $CN + H_2$ Bimolecular Reaction," Opt. Comm., 18, 128 (1976).
- 10) O. Kafri and M. J. Berry, "A New Empirical Potential Hypersurface for Bimolecular Reaction Systems," Faraday Disc. Chem. Soc., 62, XXX (1976).

- 11) R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry, "An Intracavity Dye Laser Technique for Spectroscopic and Kinetic Measurements of Transients," in J. I. Steinfeld (editor), Electronic Transition Lasers, Vol. 2 (MIT Press, Cambridge, MA, 1977).
- 12) R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry, "Measurement of Highly Forbidden Optical Transitions by Intracavity cw Dye Laser Spectroscopy," Chem. Phys. Letters, 47, 213 (1977).

The following paper with emphasis on a non-AFOSR program area was also published:

- O. Kafri, "Suggestion for a New Two-Photon Cross-Section," Chem. Phys. Letters, 36, 624 (1975).

B) Abstracts and/or Introductions

- 1) M. J. Berry, "The $F + H_2$, D_2 , HD Reactions: Chemical Laser Determination of the Product Vibrational State Populations and the $F + HD$ Intramolecular Kinetic Isotope Effect," *J. Chem. Phys.*, **59**, 6229 (1973).

$F + H_2$, D_2 , HD reactions: Chemical laser determination of the product vibrational state populations and the $F + HD$ intramolecular kinetic isotope effect*

Michael J. Berry

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706
(Received 13 July 1973)

Relative gain coefficients of individual $HF^1(DF^1)$ laser transitions in the $F + H_2$, D_2 , HD chemical lasers have been measured by a grating selection technique. Product vibrational population inversions N_v/N_{v-1} were calculated from these measurements. The results indicate a complete parallelism in product vibrational energy content in the four room-temperature isotopic reactions, modified only by a threshold effect for $HF^1(v=3)$ production in the $F + HD$ reaction and by secondary mass effects in the HF -producing vs DF -producing reactions. A room-temperature measurement of the intramolecular kinetic isotope effect in the $F + HD$ reaction is reported. Lastly, evidence is presented for highly efficient energy-transfer processes [$V \rightarrow V'$: $HF^1(v=3) + HD(v=0) \rightarrow HF^1(v=2) + HD^1(v=1)$ and $E \rightarrow V$: $I^0(5^1P_{1/2}) + HF^1(v) \rightarrow I(5^2P_{3/2}) + HF^1(v+2)$].

- 2) M. J. Berry, "Hot-Atom Initiated Chemical Laser Study of the $H^* + SF_6$ Reaction," *Chem. Phys. Letters*, **22**, 507 (1973).

HOT-ATOM INITIATED CHEMICAL LASER STUDY OF THE $H^* + SF_6$ REACTION†

Michael J. BERRY

Department of Chemistry, University of Wisconsin,
Madison, Wisconsin 53706, USA

Received 31 July 1973

Chemical laser methods have been used to study the "hot-atom" reaction: $H^* + SF_6 \rightarrow$ products at $KE_{rel} < 102$ kcal mole⁻¹. Collision-induced dissociation of SF_6 by H^* is the dominant reaction channel. Internal excitation of SF_6 may be required to promote the abstraction reaction: $H + SF_6 \rightarrow HF + SF_5$.

- 3) M. J. Berry, "Golden Rule Calculation of Reaction Product Vibronic State Distributions," *Chem. Phys. Letters*, **27**, 73 (1974).

GOLDEN RULE CALCULATION OF REACTION PRODUCT VIBRONIC STATE DISTRIBUTIONS*

Michael J. BERRY

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

Received 9 April 1974

A resonance decay model of bimolecular exchange reactions successfully treats product vibronic state distributions. Product vibronic population inversions are controlled by the extent of product structural change which occurs as reaction energy is released.

- 4) M. J. Berry, "The Chloroethylene Photochemical Lasers: Vibrational Energy Content of the HCl Molecular Elimination Products," *J. Chem. Phys.*, **61**, 3114 (1974).

Chloroethylene photochemical lasers: Vibrational energy content of the HCl molecular elimination products*

Michael J. Berry

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

(Received 30 May 1974)

Chemical laser techniques have been used to determine relative photochemical product yields and HCl($v' \leq 4$) photoelimination product vibronic state distributions resulting from chloroethylene ($\text{CH}_2=\text{CHCl}$, $\text{CH}_2=\text{CDCl}$, $\text{CH}_2=\text{CCl}_2$, *cis*- and *trans*- $\text{CHCl}=\text{CHCl}$, and $\text{CHCl}=\text{CCl}_2$) photolyses at $\lambda \geq 1550 \text{ \AA}$. The observed highly nonstatistical product vibronic state distributions are successfully matched by a bootstrap reaction dynamics model which considers sudden structural distortion and intramolecular relaxation of HCl as it separates from acetylene or haloacetylene products. Chloroethylene vacuum ultraviolet absorption spectra ($\lambda \geq 1400 \text{ \AA}$) are also reported. All available spectroscopic, photochemical, and product energy partitioning data are used to formulate a state-to-state photochemical reaction mechanism for HCl photoelimination from the chloroethylenes.

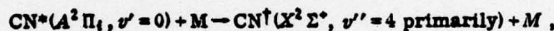
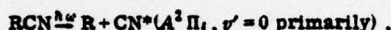
- 5) G. A. West and M. J. Berry, "CN Photodissociation and Predissociation Chemical Lasers: Molecular Electronic and Vibrational Laser Emissions," *J. Chem. Phys.*, **61**, 4700 (1974).

CN photodissociation and predissociation chemical lasers: Molecular electronic and vibrational laser emissions*

Gary A. West and Michael J. Berry

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706
(Received 17 July 1974)

Molecular electronic [$\text{CN}^*(A^2\Pi_{1/2}, v' = 0) \rightarrow \text{CN}(X^2\Sigma^+, v'' = 0, 1, 2)$] and vibrational [$\text{CN}^*(X^2\Sigma^+, v' = 5, 4, 3, 2) \rightarrow \text{CN}(X^2\Sigma^+, v'' = 1)$] cyanide radical laser emissions have been observed following photodissociative and predissociative fragmentation of cyanide parents [HCN, ClCN, BrCN, ICN, $(\text{CN})_2$, CH_3NC , CF_3CN , $\text{C}_2\text{F}_3\text{CN}$] at $\lambda \geq 1550 \text{ \AA}$. The observed transitions and their relative gain coefficients and quenching behaviors are used in connection with spectroscopy and fluorescence experiments to formulate a state-to-state photochemical reaction mechanism, viz.,



in which nascent photochemical products are formed with high electronic population inversion [$N_{\text{CN}^*(A^2\Pi_1)}/N_{\text{CN}^*(X^2\Sigma^+)} > 1$] and no vibronic inversion within the $A^2\Pi_1$ manifolds (i.e., $v = 0$ is the principal product vibronic state). Near-resonant collision-induced intersystem crossing is shown to preferentially populate $v'' = 4$ within the $X^2\Sigma^+$ electronic manifold. Electronic and vibronic population inversions are treated via state-to-state adiabatic correlation diagrams and a simple dynamical model for reaction product vibronic state distributions. Anomalous laser behavior in the BrCN photodissociation system is rationalized via an intramolecular near-resonant $E \rightarrow E'$ energy transfer scheme.

- 6) U. Dinur, R. Kosloff, R. D. Levine, and M. J. Berry, "Analysis of Electronically Nonadiabatic Chemical Reactions: An Information Theoretic Approach," *Chem. Phys. Letters*, **34**, 199 (1975).

ANALYSIS OF ELECTRONICALLY NONADIABATIC CHEMICAL REACTIONS: AN INFORMATION THEORETIC APPROACH*

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Received 9 April 1975

A practical procedure for the determination of branching ratios for reactions which lead to either excited or electronically ground state products is outlined. The method is applied to four reactions which could (on energetic grounds) produce an electronically excited iodine atom. No case of a complete inversion is found, but one reaction ($\text{F} + \text{HI}$) is predicted to yield a statistical, (one half), $I^*(^2P_{1/2})$ to $I(^2P_{3/2})$ ratio.

- 7) M. J. Berry, "Laser Studies of Gas-Phase Chemical Reaction Dynamics,"
Ann. Rev. Phys. Chem., 26, 259 (1975).

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ANNUAL REVIEW OF PHYSICAL CHEMISTRY
Volume 26, 1975

LASER STUDIES OF GAS PHASE CHEMICAL REACTION DYNAMICS¹ * 2608

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INTRODUCTION

This perspective is addressed primarily to active reaction dynamicists (i.e. chemical kineticists working on a reactant state to product state level of inquiry) to outline current capabilities of coherent light sources for the detailed study of chemical rate processes, to record past successes, and to identify future areas of important and likely progress. We assert that the following axioms, already well known to time-independent spectroscopists, also apply to time-dependent measurements of evolving reactant-product systems: (a) any matter-radiation interaction can be studied better with a coherent, rather than an incoherent, light source, and (b) coherent light sources of nearly ultimate (i.e. uncertainty principle limited) frequency and time resolution are currently available or will soon be developed for the entire energy spectrum appropriate to chemical interactions. It is now timely and meaningful for every dynamicist to inquire whether existing experiments can be improved via laser devices and, indeed, whether totally new and highly refined experiments are feasible.

We emphasize the state-to-state (i.e. microscopic) approach to chemical reaction dynamics; we wish to scrutinize chemical reactions on a global detailed level (1): at a given total system energy E , many reactant and product channels are open and many transition probabilities [i.e. the "rich person's" P -matrix (1)] must be considered. Of practical interest (2) to dynamicists (and others) are questions of energy requirements and energy disposal (1): e.g. (a) what is the optimal reactant internal state which promotes reaction at energy E ? and (b) what is the distribution of product internal states for a particular reactant internal state at energy E ?; as well as questions of energy redistribution: e.g. (c) are unimolecular reactants ergodic on the time scale of their fragmentation? and (d) what are the dominant collisional relaxation processes and time scales which degrade an initial nonequilibrium distribution? Laser methods aid the dynamicist in many ways: reactants can be selectively excited to particular internal states, product state distributions can be probed on time scales short and long compared to collisional relaxation times, etc. We survey these methods and their applications to gas phase reactions.

¹ Literature search completed in December 1974.

² Camille and Henry Dreyfus Foundation Teacher-Scholar, Alfred P. Sloan Foundation Research Fellow.

³ Our own laser studies are supported by the Directorate of Chemical Sciences, US Air Force Office of Scientific Research under Grants AFOSR-73-2423 and AFOSR-74-2666.

- 8) M. J. Berry, "Chemical Laser Studies of Energy Partitioning into Chemical Reaction Products," in R. D. Levine and J. Jortner (editors), Molecular Energy Transfer (Wiley, New York, 1976).

Chemical Laser Studies of Energy Partitioning into Chemical Reaction Products

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ABSTRACT

Chemical laser techniques for the determination of energy partitioning into individual degrees-of-freedom of chemical reaction products are reviewed. Selected studies are described and, in addition, all energy partitioning results derived from chemical laser investigations of bimolecular, unimolecular and photochemical reactions (complete through December 1973) are tabulated.

- 9) G. A. West and M. J. Berry, "A Polyatomic Chemical Laser: Vibrationally Excited Hydrogen Cyanide Produced by the $\text{CN} + \text{H}_2$ Bimolecular Reaction," *Opt. Comm.*, **18**, 128 (1976).

Volume 18, number 1

OPTICS COMMUNICATIONS

July 1976

**N8 A POLYATOMIC CHEMICAL LASER:
VIBRATIONALLY EXCITED HYDROGEN
CYANIDE PRODUCED BY THE $\text{CN} + \text{H}_2$
BIMOLECULAR REACTION***

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We have produced hydrogen cyanide chemical laser emission by flash photolysis of ICN/H_2 and $(\text{CN})_2/\text{H}_2$ mixtures in a Suprasil quartz reaction vessel. Photolysis of these reactants

(typical conditions: 40 torr total pressure of $1/25 \text{ RCN}/\text{H}_2$ mixtures photolyzed at 1500 J flash energy in a one-meter pathlength optical cavity) leads to the production of electronically excited $[\text{CN}^*(\text{A}^2\Pi_1)]$ and vibrationally excited $[\text{CN}^\dagger(\text{X}^2\Sigma^+, v)]$ cyanide radicals which have been characterized by their own laser emissions [1]. Vibrationally excited hydrogen cyanide is also formed in these mixtures by the elementary bimolecular chemical reaction: $\text{CN} + \text{H}_2 \rightarrow \text{HCN}^\dagger + \text{H}$. Hydrogen cyanide chemical laser emission occurs in P-branch transitions of the $(10^0_1) \rightarrow (10^0_0)$ and $(00^0_1) \rightarrow (00^0_0)$ bands near 3.0 microns and in Q-branch transitions of the $(00^0_1) \rightarrow (01^1_0)$ band near 3.8 microns with the temporal evolution displayed in fig. 1. Analysis of the relative gain coefficients of the lasing transitions [2,3] together with quenching and pulse radiolysis [4] experiments indicate that: a) a major portion of the reaction exoergicity (approximately 50%) is channeled into C-H stretch excitation of HCN, b) the bending mode (01^0_0) is not populated efficiently either by direct reaction or by vibrational relaxation of more highly excited HCN vibronic states, c) the reaction of vibrationally excited cyanide radical $[\text{CN}^\dagger(v)]$ with molecular hydrogen occurs adiabatically to form HCN product with C-N stretch excitation, and d) electronically excited cyanide radical $[\text{CN}^*(\text{A}^2\Pi_1)]$ does not react appreciably with molecular hydrogen. Dye laser probe experiments [5] are underway to study the ramifications of conclusions c) and d) in order to predict the reaction enhancement and energy partitioning characteristics of excited reactants. In addition, we are carrying out quasiclassical trajectory computations of the reaction dynamics using a new empirical potential hypersurface for the $\text{CN} + \text{H}_2$ reaction [6]. Preliminary ab initio H_2CN surface calculations [7] confirm the empirical approach.

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* This work was supported by the U.S. Air Force Office of Scientific Research under grant AFOSR-73-2423 and by the Research Corporation under a Frederick Gardner Cottrell grant.

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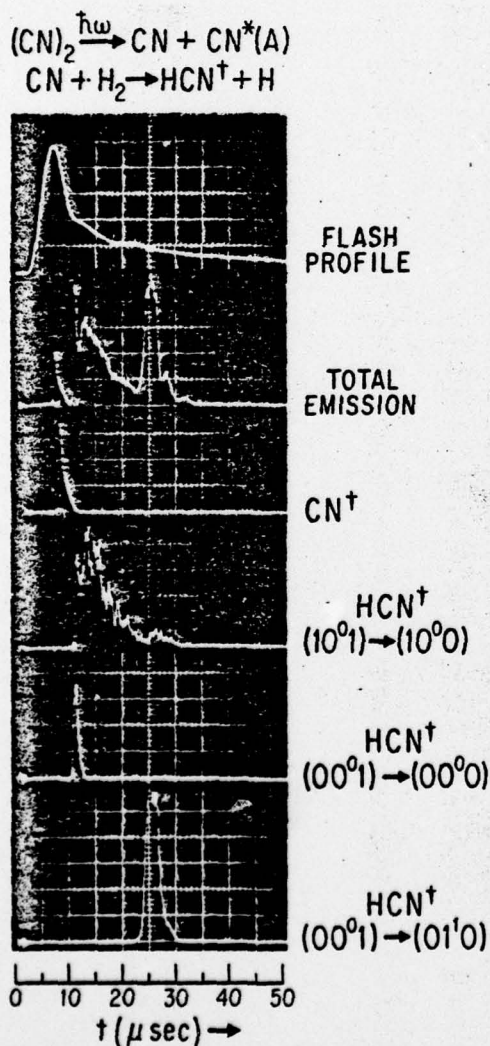


Fig. 1. Total cyanide radical and hydrogen cyanide molecular chemical laser emissions in the $(\text{CN})_2/\text{H}_2$ system. CN^\dagger and HCN^\dagger laser bands are separately shown in various traces.

- 10) O. Kafri and M. J. Berry, "A New Empirical Potential Hypersurface for Bimolecular Reaction Systems," *Faraday Disc. Chem. Soc.*, **62**, XXX (1976).

To appear as:

O. Kafri and M. J. Berry, *Faraday Disc. Chem. Soc.*, **62**, xxx (1976).

A New Empirical Potential Hypersurface for Bimolecular Reaction Systems*

* This work was supported by the Directorate of Chemical Sciences, U.S. Air Force Office of Scientific Research under Grant AFOSR-73-2423.

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Received 11 June, 1976

1. INTRODUCTION

Refined and accurate *ab initio* potential energy hypersurfaces can now be obtained for simple (i.e., few nuclei and few electrons) chemically reactive systems such as H_3 , FH_2 , and HLi_2 .¹ Certainly, the *ab initio* route is preferable to all other computational schemes in cases demanding modest expense (e.g., less than \$10 000 in 1976 U.S. dollars) for the several hundred hypersurface points required to yield a good fit to chemically interesting regions of the surface. Nevertheless, the popularity of semi-empirical surfaces of the LEPS (London-Eyring-Polanyi-Sato) and DIM (Diatomics-In-Molecules) varieties attests to the continuing utility of inexpensive (albeit of indeterminate accuracy) surfaces in practical contexts (e.g., quasiclassical trajectory studies of reaction dynamics).

We here present a fully empirical scheme for the computation of potential hypersurfaces for triatomic bimolecular reaction systems. The following sections describe our empirical approach, calibrate its accuracy by comparison to the best available H_3 *ab initio* ground potential hypersurface, and comment upon extensions and limitations of the method.

- 11) R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry,
 "An Intracavity Dye Laser Technique for Spectroscopic and Kinetic
 Measurements of Transients," in J. I. Steinfeld (editor),
Electronic Transition Lasers, Vol. 2 (MIT Press, Cambridge, MA, 1977).

AN INTRACAVITY DYE LASER TECHNIQUE FOR SPECTROSCOPIC
 AND KINETIC MEASUREMENTS OF TRANSIENTS

by: R. G. Bray², W. Henke, S. K. Liu, K. V. Reddy²,
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The intracavity dye laser technique for monitoring transient absorptions^{1,2} and small gains³ on individual rovibronic transitions is ideally suited for the study of potential new electronic chemical lasers, laser-induced or enhanced chemistry and model chemical reactions of particular interest to the theorist. Nascent product state population distributions and their subsequent temporal evolution can be monitored in reactions which may lead to electronic population inversions suitable for the production of efficient electronic chemical lasers. The high energy and temporal resolution of our apparatus and first forays in this area will be described.

- 12) R. G. Bray, W. Henke, S. K. Liu, K. V. Reddy, and M. J. Berry,
 "Measurement of Highly Forbidden Optical Transitions by Intracavity
 cw Dye Laser Spectroscopy," *Chem. Phys. Letters*, 47, 213 (1977).

MEASUREMENT OF HIGHLY FORBIDDEN OPTICAL TRANSITIONS
 BY INTRACAVITY CW DYE LASER SPECTROSCOPY†

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Received 7 January 1977

Intracavity cw dye laser quenching has been used to observe extremely weak optical transitions near 6300 Å: the 2, 0 band of the red atmospheric system of molecular oxygen and the 6,0 overtone band of HCl. Sensitivity tests indicate that band systems with oscillator strengths less than 10^{-12} can be detected readily, thereby suggesting routine use for high-resolution optical spectroscopy of forbidden transitions.

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Michael J. Berry		AFOSR-73-2423
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
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Final Scientific Report for Grant AFOSR-73-2423		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Laser Molecular reaction dynamics Photochemistry Chemical laser Unimolecular reactions Bimolecular reactions Energy transfer Spectroscopy		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
<p>Chemical laser techniques have been used to analyze energy partitioning and chemical reaction dynamics in elementary bimolecular, unimolecular, and photochemical reaction systems. Several new chemical laser systems (e.g., cyanide radical molecular electronic lasers, a hydrogen cyanide polyatomic chemical laser, and a "hot-atom" initiated bimolecular reaction laser) were discovered. A general method for the quantitative determination of product vibrational state distributions was developed and applied to many chemical (over)</p>		

20. Abstract (continued)

laser systems. Important rate processes such as specific energy partitioning leading to population inversions plus energy redistribution steps that modify nascent population inversions were determined for operating chemical lasers.

Support experiments in areas of vacuum ultraviolet spectroscopy using a synchrotron radiation source and of tunable intracavity cw dye laser spectroscopy were also carried out.

Certain theoretical approaches toward reaction dynamics were also pursued. A dynamical model for energy partitioning into specific product vibrational states was devised and applied to reaction and relaxation systems. Information theoretic methods were used to analyze patterns of energy partitioning and to predict electronic branching ratios. In addition, ab initio and empirical methods were applied to the computation of potential energy hypersurfaces for chemically reactive systems.

Additional paper completed under AFOSR sponsorship:

O. Kafri, "Suggestion for a New Two-Photon Cross-Section," Chem. Phys. Letters, 36, 624 (1975).

SUGGESTION FOR A NEW TWO-PHOTON CROSS SECTION

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Received 1 August 1975

We suggest a new two-photon (TP) absorption cross section which is independent of the wavelength of the two laser beams. The different wavelengths may cause changes in the regular cross section by orders of magnitude in the same absorbing molecule. This effect is *not* due to the resonance term, but to the number of modes.